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<p>(54) Title: PRESERVATIVE FOR WOOD, TREATING SOLUTIONS AND USE OF THE PRESERVATIVE (57) Abstract  A preservative for treating of wood, woodbased products or similar organic fibreproducts which includes one or more copper salts and perhaps zinc salts of weak organic acids, a stabilising chemical selected among the ammonium salt of a weak organic acid or a mixture of such an ammonium salt and an alkali metal salt of a weak organic acid, nitrite plus perhaps further admixture - and/or aid chemicals, where the preservative contains 0.1-1.0 parts by weight of nitrite calculated as sodium nitrite per 1.0 parts by weight of copper salt and perhaps zinc salt, calculated as copper acetate. The solution has a pH-value of 5.2-6.2 and contains at least 0.2 % by weight of ammonium - and alkali metal salt of weak organic acids. The preservative ensures a good fixation of the copper and prevents like that the leachability of it.</p>		

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## PRESERVATIVE FOR WOOD, TREATING SOLUTIONS AND USE OF THE PRESERVATIVE

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This invention relates to a preservative for treating of wood, wood based products or similar organic fibre products, which include one or more copper salts and perhaps zinc salts of weak organic acids, a stabilising chemical selected among the ammonium salt of a weak organic acid or a mixture of such an ammonium salt and an alkalimetal salt of a weak organic acid, nitrite plus perhaps further admixture - and/or aid chemicals. The treating solution has a pH-value of 5,2-6,2.

10

Treatment of wood and wood-based products to make it resistant against biological decomposition uses normally a preservative in the form of a chemical solution.

20

It has for a long time been known that copper - as well as zinc salts have protecting qualities and are very suitable for use in preservatives.

25

Earlier using of preservatives in the form of acid solutions of chromium, copper and arsenic or ammoniacal solutions of copper- and arsenic salts was widespread.

30

Such preservatives are satisfactory concerning protection of the wood but are combined with the disadvantage, that they contain chromium and arsenic, which both are harmful to the environment and the health.

35

Concurrently with the growing attention to the consequence for the environment and the health by using such preservatives you have tried to find less poisonous alternatives. So, to day you know a serie of alternative preservatives based on different copper -and/or zinc salts. From JP-application number 25.363/81 you know a preservative containing 15-25 % boric acid, 30-40 % sodium chlorid, 5-12 % zinc formate or copper formate and 5-15 % zinc acetate or copper acetate possible in mixing with

triethanoamine.

5

From EP number 58.142 you know a preservative for treating of wood in the form of an aqueous ammoniacal solution containing copper and/or zinc plus quaternary ammonium compounds.

- 10 From US patent number 4.929.454 you know an aqueous, ammoniacal arsenic-free preservative for treating of wood containing a quaternary ammonium compound and a metallic cation, selected among copper and zinc.

- From US patent number 4.857.322 you know a preservative for wood based on a copper compound, an aliphatic carboxylic acid plus a polyamine. The copper compound is preferably copperoxid, copperhydroxid or copper carbonate, the aliphatic carboxylic acid is preferably 2-ethylhexanoic acid or isooctanoic acid and  
20 the polyamine is preferably 1,3-diaminopropane.

- Although the above mentioned preservatives give good protection of the wood, they all have to a more or less degree the disadvantage, that you have a high degree of leaching of the  
25 metals from the treated wood, as the metals are not fixed to the wood, but exist in the wood as a precipitated metal salt.

- DK application number 1432/87 corresponding to EP number 238.049 deals with a preservative in the form of an aqueous  
30 solution of a copper-II-compound in the form of a complex with ammonia, an amine, an organic hydroxycarboxylic acid or a mixture of this plus a compound with an anion, which in the wood transfers the copper compound to a precipitated, stable copper-I-compounds. As an example of such compounds with anions  
35 is mentioned thiocyanate and iodide. Moreover the preservative may contain a reduction chemical, which assists in the reduction of the copper-II-compound to the copper-I-compound. As an example of such a reduction chemical is mentioned glucose. The preservative has a low copper content from about 7-11.5 % and

5

so it will have to be used in a high concentration. Further the preservative contains amines, which to day many peoples call in question from environmental reasons. Also in this preservative the copper is not fixed to the wood, but precipitated as a copper compound.

10

The authorities in the different countries have in the latest years intensified the demands on leaching from the treated wood. Thus, there is a need for preservatives, which will give a better fixation of the active ingredients and with this a decrease in leaching.

20

From WO number 91/11306 you know a copper based preservative, which for increasing the fixation of the copper ions contains a big amount of nitrit. In the application states that the fixation is best at a weak acid pH-value, but in spite of this it is stated that the pH-value shall be higher than 6.5 and preferably higher than 7.0, compare claim 1 and claim 2. This is explained by having in the preservative an increased tendency to development of  $\text{NO}_x$ -emission the lower the pH-value is, and it is illustrated by a comparison test. In other words in the application is expressed a prejudice against to use nitrite containing preservatives at a pH-value lower than 6.5. To avoid precipitation of the cation as a water insoluble alkaline salt when the pH is higher than 6.5, WO 91/11306 states, that you per one mole of the catione have to use at least four moles of a complexing agent, it means minimum 80 per cent by weight calculated on the metal salt. As the complexing agent keeps the metal in a soluble form you have to use more nitrite to achieve the same degree of fixation as without the complexing agent, compare page 5-6 and page 18-19. Therefore, WO 91/11306 states as preferred amount 2.0 to 3.0 parts by weight of biocide cation, it is copper ion and perhaps other biocide cations or

35

- 5 expressed as salts 1-1.5 parts by weight of sodium nitrite per 1 part by weight of copper acetate or 1.25-1.90 parts by weight of sodium nitrite per 1 part by weight of sodium sulfate anhydrous.
- 10 Among conventional copper based preservatives experts distinguish between acid and alkaline preservatives as the character of the copper component is essentially different in the two fields. Thus, the copper in the acid preservatives usually will be soluble while you in the alkaline preservatives usually will
- 5 need a complexing agent to soluble the copper compound. Thus in practice you have to add a complexing agent to the alkaline preservatives, for instance in the form of amines, which from an environmental point of view is seen as less desirable.
- 20 Experience-based you have an essential difference between the acid and alkaline preservatives. However the remaining compounds can have an essential influence so you cannot always say anything in general of the quality of this two types of preservatives. However, among the approved preservatives it is so,
- 25 that the copper amount in the acid preservatives can be something lower than in the alkaline preservatives, it is 3 kg copper per 1 m<sup>3</sup> sapwood when using acid preservatives against min. 4 kg copper per 1 m<sup>3</sup> sapwood when using alkaline preservatives, both for wood in ground contact.
- 30 From SE-application number 466.094 you know a weak acid preservative for treating of wood, containing copper acetate and zinc acetate, with a content of copper acetate of at least 45 % of the total amount of copper -and zinc acetate. The preservative
- 35 may, for restraining of the corrosion on the treating plant, contain alkali- or ammonium nitrite or alkali- or ammonium acetate in an amount up to 0.1 % by weight of the treating solution.



5      Acid copper salts is even in low concentrations, it means less than 2 %, strong corrosive against iron and steel and for that reason it cannot be used in practice without addition of aid compounds, which neutralize the corrosive effect.

10      In spite of a low solubility in water of the mentioned copper- and perhaps zinc salts the leaching of the copper- and the zincions from the treated wood is considerable and, therefore, the use of these will from ecological and environmental reasons need better fixation. Thus it is desirable to add a suitable aid compound to such preservatives for improving the fixation.

15      Among experts it is considered as important, that you have acid as well as alkaline preservatives available, so you have the possibility to solve different tasks. By solution of such tasks you have to consider many different things, for instance the  
20      species, the treating method, the use of the treated wood and especially the geographical variations in climate and soil.

25      When you choose between an acid and an alkaline preservative also the practical conditions play a role as the different preservatives demand different treating plants. For instance, alkaline preservatives will frequently give corrosion in case of bronze fittings and acid preservatives especially chromium-free preservatives give heavy corrosion problems against iron and steel. In other words, you cannot just like that go to an  
30      other type of preservative in an existing plant. Thus, you still have a need for a weak acid water soluble preservative on the basis of non-toxic compounds with a low degree of leaching of the metals from the treated wood.

35      As mentioned earlier it is known, that preservatives on the basis of weak acid copper- and zinc salts with a sufficiently high copper content will give good protection of wood in ground contact. You will have a high copper content, when you use a copper salt of an organic acid with low molecular weight with

5 small amount of aid chemicals for stabilising of the copper salt solution.

The above mentioned copper salts have in an aqueous solution a more or less stark blue colour. After treating the wood-based  
10 products will have a colour, which vary from nearly invisible to a stark blue colour. Such an appearance is unacceptable. Thus you have to add one or more compounds, which change the colour to a green nuance and at the same time give an identical and recognizable colour intensity.

It has been known for many years, that we have fungies, who are able to decompose treated wood with a high copper content. These fungies are called copper-tolerant fungies. To protect against decomposition caused by these fungies an unacceptable  
20 high copper loading in the wood is needed. Therefore, the preservative must in environments, where these fungus are found, be added a compound which ensures, that the wood is protected in these cases.

25 The present invention relates to a preservative for treating of wood, wood-based products or similar organic fibre products, which include one or more copper salts and perhaps zinc salts of weak organic acids, a stabilising chemical selected among the ammonium salt of a weak organic acid or a mixture of such an  
30 ammonium salt and an alkali metal salt of a weak organic acid, nitrite plus perhaps further admixture - and/or aid chemicals characterised by containing 0.1-1.0 parts by weight of nitrite, calculated as sodium nitrite per 1.0 parts by weight of copper salt and perhaps zinc salts calculated as copper acetate. The  
35 preservative in the treating solution has a pH-value of 5.2-6.2 and the amount of nitrite calculated as sodium nitrite comes to at least 0.15 % by weight of the treating solution and the stabilizing chemical is found in an amount of at least 0.2 % by weight calculated as ammonium acetate of the treating solution,

where the concentration of the ammonium salt calculated as  
5 ammoniumacetate must not exceed

$0.07 \times \frac{1}{a} \%$  by weight of the treating solution,  
where  $a$  is the concentration of nitrite calculated as sodium  
10 nitrite in per cent of the treating solution and where the  
nitrite exists in one packing unit divided from an other  
packing unit containing the remaining chemicals.

It is preferred that the copper salt is selected among copper  
15 formate, copper acetate and copper propionate or a mixture of  
these and that the zinc salt, if it is present, is selected  
among zinc formate, zinc acetate and zinc propionate or a  
mixture of these.

20 The content of nitrite in the preservative has two functions.  
So, the content causes, that the leaching of the copperions and  
the zincions from the treated wood is reduced essentially.  
Further it reduces the corrosion on the treating plant from the  
treating solution.

25 The copper salt is as mentioned preferably selected among  
copper formate, copper acetate and copper propionate or mix-  
tures of these. In a preferred version the copper salt is  
copper acetate. The active ingredient in the preservative is as  
30 mentioned mainly the copper salt or a mixture of a coppersalt  
and a zinc salt, where the zinc salt comes to 25 % of this. The  
amount of the remaining chemicals such as nitrite is adjusted  
according to the amount of the active ingredient, it is the  
amount of copper salt and perhaps zinc salt plus the degree of  
35 fixation which is wanted. However, the content of nitrite  
calculated as sodium nitrite must for the sake of protection  
against corrotion at least comes to 0.15 % by weight of the  
treating solution. The amounts in this case is calculated from  
the molecular equivalence which corresponds to the correspon-  
40 ding amount of copper acetate.

5 The nitrite is selected among the alkalimetal nitrites, it is potassium- and sodium nitrite, ammonium nitrite or a mixture of these. Sodium nitrite is preferred.

10 The amount of nitrite comes to at least 0.1 and particularly preferred is at least 0.15, especially at least 0.2 parts by weight, calculated as sodium nitrite per 1.0 part by weight of copper salt and perhaps zinc salt calculated as copper acetate and preferably most 0.8 and particularly preferred most 0.7, more preferred most 0.65 and particularly most 0.55 parts by weight calculated as sodium nitrite per 1.0 parts by weight of coppersalt and perhaps zinc salt calculated as copper acetate. At the same time you have to take care that the amount of nitrite calculated as sodiumnitrite must comes to at least 0.15 % by weight and preferably at least 0.20 % by weight of the treating solution to prevent corrosion of the treating plant.

25 The preservative according to the invention contains as mentioned a stabilising chemical selected among the ammonium salt of a weak organic acid or a mixture of such an ammonium salt and an alkalimetal salt of a weak organic acid in an amount of at least 0.2 % by weight calculated as ammonium acetate of the treating solution. As an example of usable weak organic acids you can mention formic acid, acetic acid and propionic acid or a mixture of these, preferably acetic acid. As alkali metal salt is preferably used sodium acetate.

30 The addition of the ammoniumsalt and in some cases also alkali-metal salt causes a stabilising of the treating solution by preventing precipitation of the usable chemicals and together with the nitrite it prevents corrosion of the treating plant. Further these added chemicals cause that the treated timber will have a more attractive and uniform colour. The ammonium salt is the most effective of the mentioned stabilising chemi-

cals and, therefore, it is preferably used. However, at a high content of nitrite the tendency to decomposition of the ammonium salt is increased and as a consequence some nitrogen may be generated. In these cases it is suitable to replace parts of the ammonium salt with the alkalimetal salt.

The concentration of the ammonium salt calculated as ammonium acetate must not exceed

$$0.07 \times \frac{1}{a} \% \text{ by weight of the treating solution,}$$

where  $a$  is the concentration of nitrite calculated as sodium nitrite in per cent by weight of the treating solution. Thus the necessary amount of the stabilizing chemical must at high nitrite content be supplemented by addition of the alkalimetal salt so that the total amount of the stabilizing chemical calculated as ammonium acetate comes to at least 0.2 % by weight calculated on the treating solution.

Further, the preservative contains profitably boric acid in an amount until 30 % by weight, preferably until 15 % by weight, such as 1-10 % by weight calculated on the content of copper salt and perhaps zinc salt calculate as copper acetate.

The preservative has a pH-value of 5.2-6.2 preferably 5.5-6.1 and particularly preferred 5.8-6.1 which will increase the biocidal effect of the copper and ensure a good fixation. Without addition of acid the pH-value of the treating solution is relatively constant and only to a low degree dependent on the concentration of the nitrite and the ammonium salt. In general the pH-value increases with increasing concentration of the nitrite in the treating solution and with decreasing total concentration of the treating solution. On the other hand the pH-value decreases with increasing concentration of ammonium-salt and acid. If it is wanted you can add a weak organic

acid as acetic acid for adjusting of the pH-value and for  
5 stabilising the treating solution, preferably most in an amount  
until 0.1 % by weight, calculated as acetic acid, of the  
treating solution.

Further the preservative can profitably contain a quaternary  
10 ammonium compound for instance in an amount of 15-25 % by  
weight calculated on the copper content. Quaternary ammonium  
compounds have a wide biocidal effect and thus it is able to  
support the effect of the copper and perhaps the zinc. The  
addition of the quaternary ammonium compound, for instance in  
an amount of 15-25 % by weight calculated on the copper content  
in the preservative is relevant when treating wood products for  
use in environments where copper tolerant fungies is present.  
The quaternary ammonium compounds have a wide biocidal effect  
and thus they will support the effect of the copper and the  
20 zinc and more especially be effective against the copper to-  
lerant fungies. So, when you add a quaternary ammonium compound  
to the preservative you can use less preservative which from an  
environmental as well as on economic point of view is an  
advantage. As an example of very suitable compounds can be  
25 mentioned di-cocos-di-methyl-ammonium chloride.

In a preferred version the preservative according to the  
invention has the following composition:  
30 30-80 % by weight of the copper salt, calculated as copper  
acetate,  
0-20 % by weight of the zinc salt, calculated as zinc acetate,  
6-33 % by weight of nitrite, calculated as sodium nitrite,  
2-16 % by weight of the acid ammonium salt, calculated as  
ammonium acetate,  
35 0-20 % by weight of the alkalimetal salt, calculated as sodium  
acetate,  
0-6 % by weight of the quaternary ammonium salt,  
0-15 % by weight of boric acid, especially 1-10 % by weight of  
boric acid and

5     0-5 % by weight of a weak organic acid calculated as acetic acid.

10     The copper salt and perhaps the zinc salt plus the ammonium salt will exist in one from the nitrite separated packing unit and shall be diluted with water and mixed just before use.

The preservative according to the invention can be based on the copper salt alone but if wanted it can contain up to 25 % by weight of zinc salt calculated on the total amount of copper salt and zinc salt.

20     The invention includes a treating solution which is characterised by containing 1-20 preferably 1-12 % by weight of the preservative according to the invention and 80-99, preferably 88-99 % by weight of water.

Detailed description of the invention.

25     In general the copper salt gives a good protection and it has a wide biocidal effect. Thus the preservative according to the invention can be used for many species and for many different purposes. Further, the copper salts have the advantage, that they fixe better to the wood compared to the zinc salts. However in some cases it is desirable to supplement the copper salt with other biocidal compounds as zinc salts and quaternary ammonium compounds.

30

35     It has appeared, that you, when adding a relatively small amount of nitrite, it is 0.1-1.0, preferably 0.15-0.80 parts by weight calculated as sodium nitrite per 1 part by weight of the copper salt calculated as copper acetate, essentially reduces the leaching of the copper from the timber compared to the leaching from corresponding weak acid copper based preservatives without or with a very low content of nitrite, it is such

preservatives which is described in the mentioned SE number  
5 466.094.

As it is wellknown among experts, the nitrite also has the  
advantage, that it restrains the corrosion. Thus, the preserva-  
tive is particularly usable in treating plants.

10

To improve the restraining effect against corrosion, stabili-  
sing the chemical and gives the treated timber a more attrac-  
tive colour, the preservative contains additional ammonium -  
and perhaps alkalimetal salts of weak organic acids in an  
5 amount of at least 0.2 % by weight, calculated as ammonium -  
acetate, of the treating solution.

The content of ammonium - and perhaps alkalimetal salts in the  
mentioned amount is essential as the content causes a transfor-  
20 mation of perhaps free copperions to cuprations at which the  
corrosive effect of the copperions to iron and steel disappears  
at the same time as the solubility of the copper salt is  
essentially increased.

25 The amounts of the ammoniumsalt and perhaps the alkalimetal  
salt is calculated in every case from the molecular equivalent  
which corresponds to the corresponding amount of ammoniumaceta-  
te. If you use a mixture of for instance ammoniumacetate and  
sodiumacetate, it is not necessary to adjust in practice  
30 because of the small difference in molecular weight between  
these components when calculating the amount of sodiumacetate.

The ammonium salt is the most preferred stabilising chemical  
but at an increasing concentration of nitrite in the treating  
35 solution you will have a tendency to generate nitrogen because  
of a decomposition of the ammonium. Thus, at a high content of  
nitrite in the treating solution it is suitable to replace a  
part of the ammonium salt with an alkalimetal salt. So the con-  
centration of the ammonium salt calculated as ammonium acetate



5 must not exceed

$$0.07 \times \frac{1}{a} \% \text{ by weight}$$

10 in the treating solution where a is the concentration of  
nitrite, calculated as sodium nitrite in per cent by weight of  
the treating solution. The factor 0.07 is calculated on danish  
climate conditions and when used in more hot climates it may in  
15 practice be necessary to keep the amount lower than this  
maximum value as the tendency to generation of gas is increased  
with increasing temperature. A corresponding phenomenon but  
with an opposite sign may be present when used in a more cold  
climate. In practice it is usual in the treating solution to  
20 use a concentration of ammonium salt calculated as per cent by  
weight of ammoniumacetate on

$$0.05 \times \frac{1}{a} \% \text{ by weight to } 0.07 \times \frac{1}{a} \% \text{ per cent by weight,}$$

25 where a is the concentration of nitrite, calculated as per cent  
by weight of sodium nitrite in the treating solution. If  
necessary an alkalimetal salt is added, so the total amount of  
the stabilising chemicals calculated as ammoniumacetate at  
30 least comes up to 0.2 per cent by weight of the treating  
solution.

Tests have shown the following in practice usable minimum -  
and maximum limits for the content of the ammonium salt cal-  
35 culated as ammonium acetate at different concentrations of  
nitrite calculated as sodiumnitrite.

40

5 10	Nitrite, calculated as per cent by weight of sodiumnitrite in the treating solution	Ammonium salt, calculated as per cent by weight of ammonium acetate in the treating solution		Total amount of ammonium - and alkali-metal salt calculated as per cent by weight of ammonium acetate in the treating solution
		max.	min.	min.
	0.15	0.45	0.30	0.30
	0.20	0.35	0.25	0.25
	0.40	0.17	0.12	0.20
	0.60	0.12	0.08	0.20
20	0.80	0.09	0.06	0.20
	1.00	0.07	0.05	0.20

Further the preservative according to the invention can in many cases with advantage contain a quaternary ammonium compound, for instance in an amount of 15-25 per cent by weight calculated on the copperions. The quaternary ammoniumcompounds have a wide biocidal effect and therefore it will support the effect of the copper and the zinc and will especially be effective against the copper tolerant fungies. The addition of quaternary ammonium compounds is especially relevant when treating wood-products for use in environments where the copper tolerant fungies exist. The addition of a quaternary ammonium-compound make it possible to use less amount of preservative than else would be necessary. This is an advantage from an environmental as well as an economic point of view. As an example of suitable quaternary ammonium compounds can be mentioned di-coco-di-methyl-ammonium chloride and coco-tri-methyl-ammonium chloride.

40

Boric acid can profitably enter the preservative according to

the invention. The boric acid can assist the fixation of the copper - and the zinc ions. Besides it contributes to protection of the wood against mould, copper tolerant fungies and insects, including termites.

Moreover the preservative can contain further conventional admixture - and/or aid chemicals. As an example can be mentioned chemicals for inhibition of corrosion and for stabilizing plus further fungicides and insecticides, dyes, pigments and trace chemicals.

When treating timber is it advantageous that the timber after treatment has a greenish colour. Further this colouring can serve as a security that the active ingredients in the preservative have totally penetrated the wood. Thus it is important for the acceptance of the users of the treated timber, that the product can be recognized as a product with a reliable and effective treatment. Especially for wood for use as claddings, as carports, fencings etc. it is of importance, that the greenish colour can be achieved. It is an advantage, too, that you can practically have the same colour when mixing wood products from the new chromiumfree treating with older chromium coloured products. Secondly, this colouring secures against a wrong use of untreated wood products for objects where use of treated timber is necessary if you will avoid occurrence of damages, for instance expensive damages of buildings.

In an essential part of the field for the nitrite content in the preservative according to the invention you will have the desired greenish colour despite that the preservative is chromium-free. In the remaining field it can be advantageous to add a supplementary dye. Usuable dyes are "Unisperse/Irgasperse Green" and "Unisperse/Irgasperse Black" from Ciba Geigy, Switzerland. The amount of dye in the treating solution will typical be around 0.1 per thousand.

The application of the preservative according to the invention

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can be done in the well-known ways, for instance coating, spraying, immersion, double vacuum, double vacuum-pressure or pressure processes as "Lowry" (empty-cell), "Bethel" (full-cell) and "Reuping". Among these processes immersion and pressure processes, especially "Lowry" and "Bethel" are preferred.

10

The concentration of the copper salt in the treating solution can vary depending on the process and the use of the timber but generally the treating solution contains 0.2 - 5 per cent by weight of copper calculated as copperacetate.

20

The content of nitrite calculated as sodium nitrite in the treating solution comes to at least 0.15 per cent by weight as mentioned above and is generally kept on 0.2-1.3 per cent by weight preferably 0.2-1.0 per cent by weight and mainly preferred is 0.26-0.70 per cent by weight.

25

To prevent biological decomposition from fungies and insects the preservative according to the invention can be used in a serie of other biodegradable organic materials, for instance textiles, ropes, racks, papers and boards plus bather, in which cases it must be applicated by means of known methods for treating of such materials.

30

The preservative according to the invention is effective regarding both to prevent growth of wood-destroying fungies as well as to remain in the wood. The addition of nitrite reduces essentially the leaching of the copper and the zinc from the wood.

35

## Example 1

5

A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	17 kg
	Copper acetate, $H_2O$	57 kg
10	Ammonium acetate	7 kg
	Sodium acetate	2 kg
	Boric acid	3 kg
	Sodium nitritrite	14 kg

5

The preservative was dissolved in water to a concentration of 2.2-2.5 per cent by weight and can be classed with the Nordic class A (Danish Standard DS 2122). The treating solution had a pH-value of 5.8

20

## Example 2

A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	16 kg
25	Copper acetate, $H_2O$	49 kg
	Ammonium acetate	14 kg
	Boric acid	3 kg
	Sodium nitrite	17 kg
	Di-decyl-di-methylammoniumchloride	1 kg

30

The preservative was dissolve to a concentration of 1.5-1.7 per cent by weight and can be classed with the Nordic class AB (Danish Standard DS 2122). The treating solution had a pH-value of 5.9.

35

5

## Example 3

A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	14 kg
10	Copper acetate, $H_2O$	44 kg
	Acetic acid	2 kg
	Ammonium acetate	2 kg
	Sodium acetate	5 kg
	Boric acid	10 kg
5	Sodium nitrite	23 kg

The preservative was dissolved in water to a concentration of 3.5 per cent by weight and is well qualified for use in territory with probability for attack from termites. The treating solution had a pH-value of 6.0.

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## Example 4

A preservative with the following composition was prepared:

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	Zinc acetate, $2H_2O$	16 kg
	Copper acetate, $H_2O$	53 kg
	Acetic acid	1 kg
	Ammonium acetate	6 kg
30	Sodium acetate	2 kg
	Boric acid	8 kg
	Sodium nitrite	14 kg

The preservative was dissolved in water to a concentration of 2.7 per cent by weight and can be classed with the DIN-Norm class 4. The treating solution had a pH-value of 5.9.

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## Example 5

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A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	14 kg
	Copper acetate, $H_2O$	45 kg
10	Ammonium acetate	11 kg
	Sodium acetate	1 kg
	Boric acid	8 kg
	Sodium nitrite	18 kg
	Di-decyl-di-methyl-ammoniumchloride	3 kg

The preservative was dissolved to a concentration of 1.8 per cent by weight and can be classed with the DIN-NORM Class 3. The treating solution had a pH-value of 6.1.

20

## Example 6

For use in class A and class AB in Scandinavia the following 3 packing units was prepared:

25		Packing A	Packing AB
	Copper acetate, $H_2O$	24.0 kg	18.4 kg
	Zinc acetate, $2H_2O$	7.5 kg	6.0 kg
	Ammonium acetate	3.0 kg	5.3 kg
	Sodium acetate	0.4 kg	
30	Boric acid	1.3 kg	1.1 kg
	Di-decyl-di-methyl-ammoniumchlorid, 50 %		0.75 kg
	Water	67 kg	67 kg

35

Packing C:

	Sodium nitrite	6.1 kg
	Water	10 kg

The treating solution for class A is prepared when you dissolve  
in 4800 ltr. of water 3 units of packing A and then add 3 units  
of packing C.

The treating solution for class AB is prepared when you dis-  
solve in 4850 ltr. of water 2 units of packing AB and then add  
2 units of packing C.

#### Example 7

A preservative with the following composition was prepared:

Copper acetate, H <sub>2</sub> O	63 kg
Ammonium acetate	4 kg
Sodium acetate	6 kg
Boric acid	2 kg
Sodium nitrite	25 kg

The preservative was dissolved in water to a concentration of  
2.1-2.6 per cent by weight and can be classed with the Nordic  
class A according to DS 2122 for wood in ground contact. The  
treating solution had a pH-value of 5.9.

#### Example 8

A preservative with the following composition was prepared:

Copper acetate, H <sub>2</sub> O	59 kg
Ammonium acetate	11 kg
Sodium acetate	4 kg
Sodium nitrite	22 kg
Di-coco-di-methyl-ammoniumchloride	4 kg

The preservative was dissolved to a concentration of 1.5-1.7  
per cent by weight and can be classed to class AB according to  
DS 2122 for wood out of ground contact. The treating solution  
had a pH-value of 6.0.



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## Example 9

A preservative with the following composition was prepared:

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Copper acetate, H <sub>2</sub> O	54 kg
Ammonium acetate	2 kg
Sodium acetate	8 kg
Boric acid	5 kg
Acetic acid	1 kg
Sodium nitrite	30 kg

20

The preservative was dissolved to a concentration of 3.2 per cent by weight and is well qualified for treating of timber for use in territory with probability for attack from termites. The treating solution had a pH-value of 5.9.

## Example 10

25 A preservative with the following composition was prepared:

Copper acetate, H <sub>2</sub> O	63 kg
Ammonium acetate	8 kg
Sodium acetate	2 kg
30 Boric acid	9 kg
Acetic acid	1 kg
Sodium nitrite	17 kg

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The preservative was dissolved in water to a concentration of 2.2 per cent by weight and can be classed to class 4 in the DIN-norm for treated wood in ground contact. The treating solution had a pH-value of 5.9.

## Example 11

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A preservative with the following composition was prepared:

	Copper acetate, H <sub>2</sub> O	56 kg
	Ammonium acetate	14 kg
10	Boric acid	9 kg
	Sodium nitrite	18 kg
	Di-coco-dimethyl-ammoniumchloride	3 kg

The preservative was dissolved to a concentration of at least  
5 1.5 per cent by weight and can be classed to class 3 in the  
DIN-norm for treated wood for use out of ground contact. The  
treating solution had a pH-value of 6.0.

## Example 12

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For use in class A and class AB in Scandinavia the following 3  
packing units was prepared:

	Packing A	Packing AB	
	Copper acetate, H <sub>2</sub> O	14.8 kg	15.7 kg
25	Ammonium acetate	0.9 kg	2.9 kg
	Sodium acetate	1.4 kg	1.1 kg
	Boric acid	0.5 kg	-
	Di-decyl-di-methyl-ammoniumchloride, 50 %	-	2.2 kg
30	Water	50 kg	50 kg

## Packing C

35	Sodium nitrite	5,85 kg
	Water	10 kg

The treating solution for class AB was prepared when you dis-

5 solve in 4700 ltr. of water 5 units of packing A and then add 5  
units of packing C. The treating solution for class AB was  
prepared when you dissolve in 4800 ltr. of water 3 units of  
packing AB and then add 3 units of packing C.

## Example 13

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A preservative with the following composition was prepared:

Zinc acetate, $2H_2O$	16 kg
Copper acetate, $H_2O$	48 kg
Ammonium acetate	3 kg
Sodium acetate	5 kg
Acetic acid	1 kg
Boric acid	5 kg
Sodium nitrite	22 kg

20

The preservative was dissolved in water to a concentration of  
2.7-3.1 per cent by weight and can be classed to class A (DS  
2122). The treating solution had a pH-value of 6.0.

25

## Example 14

A preservative with the following composition was prepared:

Zinc acetate, $2H_2O$	14 kg
Copper acetate, $H_2O$	45 kg
Ammonium acetate	12 kg
Boric acid	8 kg
Sodium nitrite	18 kg
Di-decyl-di-methyl-ammoniumchloride	3 kg

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The preservative was dissolved to a concentration of 1.7-1.8  
per cent by weight and can be classed to class AB (DS 2122).  
The treating solution had a pH-value of 6.1

## Example 15

5 A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	14 kg
	Copper acetate, $H_2O$	43 kg
	Ammonium acetate	2 kg
10	Sodium acetate	9 kg
	Boric acid	2 kg
	Sodium nitrite	30 kg

The preservative was dissolved in water to a concentration of 3.3 per cent by weight and can be classed to class 4 in the DIN-norm. The treating solution had a pH-value of 6.1.

## Example 16

20 A preservative with the following composition was prepared:

	Zinc acetate, $2H_2O$	13 kg
	Copper acetate, $H_2O$	42 kg
	Ammonium acetate	8 kg
25	Sodium acetate	5 kg
	Boric acid	9 kg
	Sodium nitrite	23 kg

30 The preservative was dissolved in water to a concentration of 1.9 per cent by weight and can be classed to class 3 in the DIN-norm. The treating solution had a pH-value of 6.1.

## Example 17

35 For use in class A and class AB in Scandinavia the following 3 packing units was prepared:

-25-

		Packing A	Packing AB
5	Zinc acetate, $2H_2O$	4.5 kg	4.1 kg
	Copper acetate, $H_2O$	13.8 kg	13.1 kg
	Ammonium acetate	0.9 kg	3.5 kg
	Sodium acetate	1.5 kg	-
	Acetic acid	0.3 kg	-
10	Boric acid	1.5 kg	2.3 kg
	Di-decyl-di-methyl	-	
	ammonium chloride, 50 %		1.8 kg
	Water	50 kg	50 kg
5	Packing C		
	Sodium nitrite	7.70 kg	
	Water	10 kg	

20

The treating solution for class A was prepared when you dissolve in 4700 ltr. of water 5 units of packing A and then add 5 units of packing C. The treating solution for class AB was prepared when you dissolve in 4800 ltr. of water 3 units of packing AB and then add 3 units of packing C.

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#### Example 18

30 The present example indicates the leaching tests for determination of the degree of leaching of the zinc- and the copperions from wood treated with different preservatives according to the invention with varied content of sodium nitrite at pH 5.8-6.1.

35 The tests was carried out on Scotch Pine (*Pinus Silvestris*), treated according to the full-cell process. After fixation the degree of leaching was determined be immersion in distilled water for 72 hours.

To ensure totally immersion of the wood samples, the air in the wood was disappeared in vacuum before immersion. The fixation in the following table 1, expressed as per cent, is determined from an analyse of the copper- and zinc content in the wood samples before the immersion and an analyse of the copper- and zinc content in the water extract.

You will find the results from the present test in the following table 1:

Components	Per cent by weight in the treating solution						
Zinc acetate, $2H_2O$	0.46	0.46	0.46	0.46	0.46	0.46	0.46
Copper acetate, $H_2O$	1.46	1.46	1.46	1.46	1.46	1.46	1.46
Boric acid	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Sodium nitrite.	*	*0.10	0.20	0.25	0.50	0.75	1.50
Fixation of copper in per cent	55	59	61	62	67	72	82
Fixation of zinc in per cent	27	28	30	31	34	38	48

#### Footnote

\* Not according to the invention - formulation for comparison.

From the table you see, that the addition of nitrite in an amount of 75 % of the total amount of copper- and zinc acetate increases the fixation of copper from 55 % to 82 % and the fixation of zinc from 27 % to 48 %.

## Example 19

- 5 The present example illustrates a test to determinate the generation of gas from a serie of different treating solutions according to the invention.

10 The determination was carried out on solutions in a closed system at a temperature of minimum 18° C for at least 3 mounths by measuring a possible increase in pressure. The concentration of copper- and zincacetate was totally 1.72-1.92 % and the concentration of boric acid was 0.22 %.

5

Table 2.

	Acetic acid	Ammonium acetate	Sodium acetate	Sodium nitrite	Generation of gas
20	-	0.10	0.10	0.20	no
	-	0.20	-	0.20	no
	-	0.20	0.20	0.40	no
	-	0.20	-	0.40	yes/no
	0.04	0.20	-	0.40	yes/no
25	0.08	0.20	-	0.40	yes
	-	0.24	-	0.48	yes
	-	0.16	0.10	0.60	no
	-	0.10	0.16	0.68	no
	-	0.20	0.56	0.72	no
30	-	0.20	0.20	0.72	yes
	-	0.20	0.60	0.76	no
	-	0.08	0.16	0.76	no
	-	0.12	0.24	0.76	yes/no
	-	0.20	0.40	0.76	yes
35	-	0.20	0.20	0.76	yes
	-	0.16	0.08	0.76	yes
	0.10	0.20	0.40	0.76	yes
	-	0.24	0.16	0.76	yes
	-	0.40	0.40	0.76	yes
40	-	0.24	-	0.76	yes
	-	0.36	-	0.76	yes
	-	0.08	0.16	0.80	no
	-	0.10	0.20	0.80	no
	0.04	0.08	0.16	0.80	no

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In the table you see, that contemporary high concentrations of sodium nitrite and ammonium acetate increases the generation of gas but if at the same time sodium acetate is added, the tendency to the generation is reduced. Acetic acid in return increases the generation. When adjusting the amount of the different components, the generation of gas is eliminated.

## Example 20

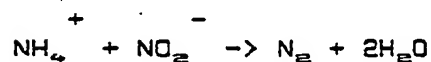
5

The present example illustrates a test to determinate the generation of gas from 2 treating solutions according to the invention.

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The possible generated type of air consists nearly totally of unpoisonous nitrogen because of the content of ammoniumions in the solution, compare the following chemical reaction:

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A possible generation of gas is directly proportional with a corresponding decrease in the concentration of nitrite ions.

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The solution was prepared in that way that the sodium nitrite was dissolved alone as a 10 % solution. The remaining components were dissolved in the remaining water and at least the 2 solutions were mixed. The treating solutions were kept at 18-20° C.

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The solutions had the following compositions:

	Per cent by weight	
	A	B
Cupri acetate, $H_2O$	1.46	0.72
Zinc acetate, $2H_2O$	0.46	0.23
Boric acid	0.07	0.04
Ammonium acetate	0.17	0.20
Sodium nitrite	0.37	0.25
Sodium acetate	0.03	-
Quaternary ammonium-chloride, 50 %	-	0.04

You will find the results in the following table 3.

	Hours after production	NO <sub>2</sub> in µg/ml		pH-value	
		A	B	A	B
	0	2513	1740	5.77	5.91
	24	2440	1718	5.76	5.90
	168	2414	1644	5.78	5.92
	720	2532	1723	5.77	5.89
	Average	2475	1706		
	Dispersion	55	60		
	Calculated concentration	2474	1667		

As you see from the table the concentration of nitrite ions are the same even at 720 h after the production. From this it can be concluded that no generation of nitrogen containing gases will take place. The above mentioned reaction is consequently

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totally stopped at the concentrations, which are used in this application for a patent. The effect of an increase of the concentration or an increase of the temperature can besides be compensated of a small addition of a mixture consisting of 3 parts of acetic acid plus 97 parts of sodium acetate, which at the same time will keep the pH-value on about 5.9, by which a maximum utilization of the nitrite ions is achieved.

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CLAIMS

5 1.  
Preservative for treating of wood, woodbased products or  
similar organic fibreproducts which includes one or more copper  
salts and perhaps zinc salts of weak organic acids, a stabili-  
10 sing chemical selected among the ammonium salts of a weak  
organic acid or a mixture of such an ammonium salt and an  
alkali metal salt of a weak organic acid, nitrite plus perhaps  
further admixture - and/or aid chemicals characterized by  
containing 0.1-1.0 parts by weight of nitrite, calculated as  
sodium nitrite per 1.0 part by weight of copper salt and  
5 perhaps zinc salt calculated as copper acetate. The preservati-  
ve in the treating solution has a pH-value of 5.2-6.2 and the  
amount of nitrite calculated as sodium nitrite comes to at  
least 0.15 % by weight of the treating solution and the stabi-  
lising chemical is present in an amount of at least 0.2 % by  
20 weight, calculated as ammonium acetate, of the treating solu-  
tion, where the concentration of the ammonium salt calculated  
as ammonium acetate must not exceed

25  $0.07 \times \frac{1}{a} \% \text{ by weight}$

of the treating solution, where  $a$  is the concentration of  
nitrite in per cent of the treating solution and where the  
nitrite exist in one packing unit divided from another packing  
30 unit containing the remaining chemicals.

2.  
Preservative according to claim 1 characterized by using as  
weak organic acid formic acid, acetic acid or propanoic acid or  
35 a mixture of this, preferably acetic acid.

3.  
Preservative according to claim 1, characterized by the nitrite  
is alkali nitrite, ammonium nitrite or a mixture of this.

4.  
Preservative according to claim 1 characterized by containing  
5 0.1-0.8, preferably 0.15-0.70 and more preferred 0.20-0.55  
parts by weight of nitrite, calculated as sodium nitrite, per  
1.0 part by weight of copper salt and perhaps zinc salt,  
calculated as copper acetate.
- 10 5.  
Preservative according to claim 1 characterized by having a pH-  
value of 5.7-6.1.
6.  
5 Preservative according to each of the previous claims charac-  
terized by containing  
35-80 % by weight of the copper salts, calculated as copper  
acetate.  
0-20 % by weight of the zinc salts, calculated as zinc acetate.  
20 6-33 % by weight of nitrite, calculated as sodium nitrite.  
2-16 % by weight of the acid ammonium salts, calculated as  
ammonium acetate.  
0-20 % by weight of the alkali metal salts, calculated as  
sodium acetate.
- 25 0-6 % by weight of a quaternary ammonium salt.  
0-15 % by weight of boric acid and  
0-5 % by weight of a weak organic acid, calculated as acetic  
acid.
- 30 7.  
Preservative according to each of the previous claims charac-  
terized by containing 0-25 % by weight of zinc salts of the  
total content of copper salts and zinc salts.
- 35 8.  
A treating solution characterized by containing 1-20, pre-  
ferably 1-12 % by weight of the preservative according to each  
of the previous claims and 80-99, preferably 88-99 % by weight  
of water.

9.

5     The application of the preservative according to each of the  
previous claims for treating of wood, wood-based products or  
similar organic fiberproducts.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00140

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B27K 3/52

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4857323 A (BROR O. HAGER), 15 August 1989 (15.08.89)  --	1-9
A	WO 9111306 A1 (HICKSON INTERNATIONAL PLC), 8 August 1991 (08.08.91)  -- -----	1-9

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/DK 95/00140

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA-A- 1284555	04/06/91
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		SE-A- 8600888	28/08/87
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